

HYDROUS PHASES IN ALH84001: FURTHER EVIDENCE FOR PRETERRESTIAL ALTERATION AND A SHOCK-INDUCED THERMAL OVERPRINT

Adrian J. Brearley, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA (e-mail: brearley@unm.edu)

Introduction: Orthopyroxenite ALH 84001 is a complex igneous meteorite that has experienced multiple episodes of shock [1-3], in addition to the formation of widely described secondary carbonates, magnetites and sulfides. The origin of these secondary phases has been debated extensively [4-11], but the involvement of a hydrothermal fluid in carbonate formation has been widely posited [5-7]. However, mineralogical evidence supporting such an origin, in the form of hydrous phases such as clay minerals, is extremely limited [12]. We have previously described the only unambiguous evidence of preterrestrial phyllosilicate phases in ALH 84001 [12]. In this case, we found platy and ribbon-like crystals of K-bearing micas, closely intergrown with carbonate in ALH 84001. These observations stimulated a search for other occurrences of phyllosilicates in ALH 84001. Here we report new observations on the occurrences of such phases that are also unambiguously of martian origin.

The formation of secondary, terrestrial clay minerals is highly probable during the long residence time of ALH 84001 in the Antarctic ice. In such a situation, the unequivocal identification of hydrous, preterrestrial alteration products is difficult, but possible [13]. However, in this study, the textural settings of the phyllosilicates and the nature of the phases present (as discussed below) allows us to place rigorous and essentially unambiguous constraints on their formation location.

Observations: The different occurrences of carbonates in ALH 84001 have been described in detail [4-11]. We have concentrated on carbonates that have clearly been disrupted and dispersed within the feldspathic glass as a result of impact processes such as melting and melt mobilization [14]. Several different regions of fragmented carbonates have been characterized in detail, using SEM, EPMA and TEM techniques. The carbonate fragments occur as angular grains ranging in size from <10 μm up to 50 μm , embedded within the feldspathic glass. In many cases, there is clear evidence of injection of feldspathic melt between the carbonate fragments [14]. The fragments sometimes retain evidence of the compositional zoning that is commonly observed in undisturbed, intact carbonate globules.

In the TEM, the carbonate fragments have planar interfaces with the feldspathic glass and the interfaces are the cleavage surfaces of carbonate rhombs. This observation provides further evidence that the fragments represent parts of disrupted carbonate grains and are not formed by infilling of vesicles within the shock glass. We have described the microstructures of the carbonate fragments and the occurrence of magnetite elsewhere [11]. Here, we focus on new observations on occurrences of phyllosilicates associated with the carbonate fragments. In all the examples we have examined, the fragments are completely entrained and surrounded by feldspathic glass.

Most carbonate fragments contain no evidence of hydrous phases. However, we have found several fragments in which variable amounts of phyllosilicates are present. In all cases, the phyllosilicates are restricted to the carbonate fragments and never extend into the surrounding feldspathic glass. The phyllosilicates are always truncated abruptly at the interface between the carbonate and the glass, although evidence of partially dehydrated phyllosilicates within the glass is sometimes present.

The occurrence of the phyllosilicates is somewhat variable. In two cases, small (<120 nm), irregularly-shaped pockets of extremely fine-grained crystals (<10 nm in width and <100 nm in length) occur within separate carbonate fragments. In one case, the pockets are associated with twin planes and in the second case, one surface of the pocket is a cleavage plane. In a third occurrence, the phyllosilicates occur in a vein that crosscuts a carbonate fragment and bifurcates. The vein (~150 nm wide) can only be traced for about 1.5 microns from the edge of the TEM foil to the edge of the fragment, but could have extended significantly further. The edges of the vein are irregular and the carbonate texture indicates that some dissolution has occurred during the vein formation.

In all these cases, the phyllosilicates are extremely fine-grained (<20 nm wide parallel to the c-axis). In the pockets, the crystallites are randomly oriented but in the vein tend to be oriented approximately normal to the vein edges. The crystallites are sensitive to the electron beam and beam damage rapidly. Basal spacings of these clays, measured from high resolution TEM images, are typically ~ 1.0 nm although some basal spacings of ~ 0.7 nm have also been recorded and interlayering of phases with these basal spaces does occur. Analytical electron microscopy of regions of the phyllosilicate shows that they are aluminous and MgO-rich ($\text{Mg}/(\text{Mg}+\text{Fe}) = 0.66\text{-}0.73$), but poor in K, with <2.5 wt% K_2O . The Si/Al ratios (atomic %) are somewhat variable, but lie in the range 3-4.5. The high Mg and as well as the 1.0 nm basal spacings are most consistent with the trioctahedral mica, phlogopite, although the mica does appear to be K-deficient. However, this may be due to volatile loss during microanalysis. In some analyses, excess Si in the tetrahedral site is present suggesting that the phlogopite may be intergrown with more illitic mica or clay minerals.

Discussion: Although formation of hydrous phases as a result Antarctic weathering is plausible, several lines of evidence suggest that this interpretation is unlikely in this case. Instead, we argue that the hydrous phases are martian in origin and provide insights into the relationship between carbonate formation and hydrous fluids. First, the phyllosilicates occur associated with carbonate fragments that are completely entrained within feldspathic glass and would therefore have been isolated from terrestrial fluids [12]. We cannot rule out the possibility that fractures

PRETERRESTRIAL HYDROUS PHASES IN ALH 84001: Adrian J. Brearley

are present that might have provided pathways for Antarctic water to gain access to the fragments. However, we think that this is unlikely because we have not observed evidence of fractures within the glass, even on the TEM scale.

Second, the occurrence of the phyllosilicates is restricted exclusively to the carbonates and never extends into the glass. This is compelling evidence that the phyllosilicates formed within the carbonates prior to fragmentation and disruption by feldspathic melt. If phyllosilicate formation had occurred within a terrestrial environment then evidence of hydrous alteration of the feldspathic glass would be expected because of the high susceptibility of glasses to alteration. However, where phyllosilicates occur there is no evidence of phyllosilicate formation within the glass itself.

Third, in some examples, we have observed evidence of local dehydration of phyllosilicates at the interface between the glass and the carbonate fragments [12]. In this region, the phyllosilicates have a curved, often undulatory morphology that is not present elsewhere. In addition, some of the phyllosilicate grains appear to be amorphous, evidence that indicates that the grains may have decomposed or begun to decompose as a result of heating caused by entrainment within the feldspathic glass.

These observations provide very strong evidence that the formation of the hydrous phases must have occurred before or possibly during the entrainment of the carbonate within the feldspathic glass. Hence a martian origin is indicated.

We have previously described one occurrence of K-bearing micas associated with carbonates in ALH 84001 [12]. We originally suggested that these micas were illitic in character, but further work shows that they are also probably phlogopitic. The new occurrences of phlogopitic mica documented here differ in a number of important respects from the first occurrence we described. In the original occurrence, the phlogopite occurs as elongate, ribbon-like crystals that are closely intergrown with the carbonate fragments [12]. The grains are subparallel and extend through the carbonate for several hundred nanometers. The crystals are generally well-ordered with no evidence of interlayering or crystal defects.

In comparison, the new occurrences of phlogopite are much finer-grained and more poorly crystalline. Compositionally, they also appear to be somewhat different in being poorer in Na and having a higher Si/Al ratio, possibly because they are intergrown with an illitic mica. In addition, the micas occur either as pockets within the carbonate or as distinct veins, rather than closely intergrown with the carbonate.

The presence of phlogopitic mica within carbonate fragments is somewhat unexpected, because this phase is formed typically at relatively high temperatures. However, we suggest that the presence of phlogopite is consistent with previous suggestions regarding the thermal history of carbonate in ALH 84001 [12,14]. We interpret the phlogopite as being the result of relatively high temperature reactions that occurred during thermal heating associated with shock melting of the feldspathic glass. Two reactions could plausibly be responsible: a) dolomite + K-feldspar + H₂O =

phlogopite + calcite + CO₂ or b) dolomite + illitic muscovite = phlogopite + calcite + CO₂. Reaction a) has been investigated experimentally [15] and occurs at temperatures between ~350 and 490°C depending on XCO₂ in the fluid phase. The presence of Fe in the carbonate will lower the activity of dolomite and hence the equilibrium temperature of the reaction. No data on reaction (b) are available, but it seems probable that it would occur at a similar or perhaps lower temperature than reaction (a).

Formation of phlogopitic mica by reaction (a) is unlikely because this reaction should occur wherever water is present at the contact between the K-bearing feldspathic glass and carbonate. However, we see no evidence of such a reaction at this interface. Reaction (b), involving a preexisting K-bearing phase, seems much more probable. The morphology of the hydrous phases and their extremely fine grain size provides strong evidence that a preexisting generation of low-temperature phyllosilicates (clays?) must have been present when the carbonates were fragmented and dispersed within the feldspathic glass. This would explain the highly localized occurrences of phlogopite, i.e. reaction (b) could only occur where appropriate reactant phases were present.

Conclusions: Although rare, hydrous phases do occur in ALH 84001 associated with carbonates, demonstrating that water-bearing fluids were present at various times in the complex history of this meteorite. The presence of phlogopite appears to be result of the breakdown of preexisting low temperature hydrous phases. Our new data indicate that more than one generation of such preexisting phases may be present associated with the carbonate minerals. One generation is closely intergrown and apparently formed contemporaneously with the carbonate [12]. The second generation, documented here, formed later, possibly during the waning stages of a hydrothermal system, or even during a completely separate event, much later in the history of ALH 84001. However, the nature of the original hydrous phases has been obscured by thermal processing as a result of shock. Shock heating caused a reaction between the early formed phyllosilicates and the associated carbonate resulting in the formation of higher temperature phlogopitic mica.

References: [1] Treiman, A.H. (1995) *Meteoritics* **30**, 294-302 [2] Mittlefehldt, D.W. (1994) *Meteoritics* **29**, 214-221. [3] Treiman, A.H. (1998) *MAPS* **33**, 753-764. [4] McKay, D.S. et al. (1996) *Science* **273**, 924-929. [5] Romanek, C.S. et al. (1994) *Nature* **372**, 655-656. [6] Valley, J.W. et al. (1997) *Science* **275**, 1633-1638. [7] Leshin, L. et al. (1997) *GCA*, **62**, 3-13. [7] Harvey, R.P. and McSween, H.Y., Jr (1996) *Nature* **382**, 49-51. [9] Scott, E.R.D. et al. (1997) *Nature* **387**, 377-379. [10] Bradley et al. (1996) *GCA* **60**, 5149-5155. [11] Brearley, A.J. (1998) *LPSC Abstract #1451*. [12] Brearley, A.J. (1998) *LPI Contribution #956*, 6-8. [13] J. L. Gooding J.L. et al. (1988) *GCA* **52**, 909-915. [14] Shearer, C.K. and Brearley, A.J. (1998) *LPI Contribution #956*, 47-48. [15] Puhar, D. and Johannes, W. (1974) *CMP* **48**, 23-31. **Acknowledgements:** This research was supported by NASA grant NAG5-4935 to A.J. Brearley, P.I.